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(54) PREPARATION OF QUICK-WATER-ABSORBING POLYVINYL ACETAL POROUS BODY

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(72) Inventor: Yoshihito Yamauchi
2-20-304 Tamagawa
Takatsuki-shi, Osaka
(71) Applicant: [illegible] Co., Ltd.
3-3-26 [illegible]
Sumida-ku, Tokyo
(74) Agent: Kouichi Mizuguchi, patent attorney

SPECIFICATION

Claim

Preparation of quick-water-absorbing polyvinyl acetal porous body, characterized in that upon preparing a polyvinyl acetal porous body by adding an aldehyde and acids into a polyvinyl alcohol solution while heating in the presence of a porous formation auxiliary agent, 1 ~ 30 wt% of polyethylene glycol having a molecular weight of 600 ~ 1,500 in the raw material solution is added to the polyvinyl alcohol.

DETAILED DESCRIPTION OF THE INVENTION

[Industrial Application Field]

The present invention pertains to the preparation of a quick-water-absorbing polyvinyl

acetal porous body.

When an aldehyde and acid (as the catalyst) are added to polyvinyl alcohol (hereinafter, it is abbreviated as PVA) and allowed to react, PVA acetalation is carried out, and a water-insoluble PVAt [polyvinyl acetal] porous body is obtained. This substance has a high chemical resistance, and the microscopic and continuous pore formation characteristics in combination with the hydroxyl group provide an excellent hydrophilic property and water absorbing property. It has broad cleaning uses, for example, it is used for car washing, house-hold dish washing, and body-wash sponges.

Although the PVAt porous body is said to have an excellent hydrophilic property and water absorbing property, it has draw materialback that when it dries out it is difficult to absorb water even when soaked in water. Therefore, it is difficult to reduce its hardness when it is dried out and it lacks practical usage applications.

As a result of concerted research on the improvement of draw materialbacks of the PVAt porous body, the present inventor has arrived at completion of the present invention. The purpose of the present invention is to provide a preparation method of a PVAt porous body that absorbs water quickly in its dried out state.

That is, it is a preparation method of a quick-water-absorbing polyvinyl acetal porous body of the present invention, characterized in that upon preparing a polyvinyl acetal porous body by adding an aldehyde and acids into a polyvinyl alcohol solution while heating in the presence of a porous formation auxiliary agent, 1 ~ 30 wt% of polyethylene glycol having a molecular weight of 600 ~ 1,500 in the raw material solution is added to the polyvinyl alcohol.

As described above, the characteristic of the present invention is the addition of polyethylene glycol to the reaction raw material liquid and allowing an acetalation reaction to occur. In the prior art, a method for impregnating the PVAt porous body in a polyvinyl alcohol solution including glycerine, sorbitan, triethylene glycol, or an alkanolamine such as triethanolamine or trimethanolamine, which is beneficial for enhancing its moisture-absorption characteristics and moisture retention properties, and for improving the softness and water absorbing properties in the dry state has been proposed.

However, the post-treatment proposed in these methods nearly lost all its effects after one usage when used as a cleaning means.

Therefore, the present inventor tried to produce a porous body by adding a polyvinyl alcohol and an alkanolamine into the reaction raw material solution in advance. However, the effectiveness of the improvement is also not long lasting.

The present inventor performed further research to find a solution with regard to the effective long-term performance, and came up with ideas that regardless of the involvement of an aldehyde, the added substance is required for binding and fixation, and concluded that the

chain length is an important element for reaction probability. Therefore, the present inventor found that polyethylene glycol with molecular weight in a specific range has excellent hemiacetal binding property, long-term performance, and quick-water-absorbing properties.

The polyethylene glycol used in the present invention can be obtained by the well-known methods: for example, the ones obtained by using ethylene glycol, glycerine as the starter, and polymerizing ethylene oxide. It is vital that the molecular weight is in a range of 600 ~ 1,500. That is, if the molecular weight is under 600, the quick-water-absorbing property with an excellent long-term performance was not observed. On the other hand, if the molecular weight is over 1,500, the water absorbing property, in particular the long-term performance of the quick-water-absorbing property, are also poor. When under and above the specified molecular weight range, the objective of the present invention is not attainable. It is required that the content is between 1 ~ 30 wt% with respect to PVA. If the content is less than 1%, the satisfactory product with a superb quick-water-absorbing property is not achievable. Also, if the content is more than 30%, it is also undesirable because of the uneven airholes and poor texture of the porous product. Therefore, the preferred content is 3 ~ 12 wt% with respect to PVA.

As the PVA used in the present invention, substances ordinarily used for manufacturing a sponge can be used. That is, preferably use is made of the ones with [illegible] between 80 ~ 98%, polymerization between 600 ~ 4,000, preferably between 1,000 ~ 2,000, and they can be properly combined.

As the airhole formation auxiliary agent used for improving homogeneity of the airholes, there are the starches and derivatives or granular matter, surfactants, wood flour, fibrin, [illegible] acid soda, etc. These can be chosen according to the purpose. The most often used are starch from the potato, yam, rice, wheat, and corn used in the original form or as their swollen [swelling agent] formulations.

Also, the aldehydes used include aliphatic and aromatic aldehydes such as formaldehyde, acetaldehyde, butyaldehyde, nonaldehyde, and benzaldehyde. However, the type of aldehyde that is especially preferred in the present invention is formaldehyde due to its cost-effectiveness. Dialdehydes such as glyoxal and adipoaldehyde [transliteration] are preferred from the aspect of excellent long-term performance and quick-water-absorbing properties.

Acids including the inorganic acids such as hydrochloric acid, sulfuric acid, phosphoric acid, and nitric acid, as well as organic acids such as acetoacetic acid are added as [illegible] for PVA acetalation by aldehydes.

An application example applying the method of the present invention and using the above mentioned raw material solution is described as follows.

First, to prepare the reaction raw material liquid, PVA is allowed to dissolve in water by heating to make a 4 ~ 18% aqueous solution. Next, 10 ~ 200 wt% of an airhole formation

auxiliary agent or its aqueous solution, or the dispersion liquid, is added and mixed thoroughly with PVA.

The aldehyde and [illegible] acid are then added to the mixed solution at 0.5 ~ 2 mol, preferably 0.8 ~ 1.5 mol with respect to PVA. Furthermore, the aforementioned prescribed polyethylene glycol is added and mixed thoroughly. Thus, the reaction raw material liquid is obtained.

Various [illegible], coloring agents, and other substances can be added to the reaction raw material liquid according to necessity.

Next, the above raw material solution is cast molded and allowed to react at 40 ~ 90°C for 1 ~ 60 hours. If the reaction temperature is lower than 40°C, it is nearly impossible for the acetalation reaction to proceed. If the reaction temperature is above 90°C, the result is undesirable because the intensified reaction will cause poor acetalation and inhomogeneous airholes. Also, if the reaction time is less than one hour, there will insufficient time for carrying out acetalation and the skeleton [backbone] of the porous body will not be formed. On the other hand, if the reaction time is too long, the output is poor. After washing the porous body obtained as described above with water and allowing it to dry, the PVAt porous body is obtained with the method described in the present invention. If necessary, place the porous body into an aqueous solution containing an aldehyde and acid before and after washing with water, then perform the heat treatment at 40 ~ 90°C for 1 ~ 40 hours, and further carry out aging or [illegible] acetalation reaction. With these treatments, the fixation property of the polyethylene glycol is improved, and a long-term quick-water-absorbing performance along with water resistance and strength properties can be improved.

The PVAt porous body produced with the method of the present invention exhibits a quick-water-absorbing property not seen in the prior art and has an excellent long-term performance, making it useful for making various cleaning applications.

Application examples of the present invention are illustrated below.

Application Example 1

Disperse 10 units of [illegible] PVA with an average degree of polymerization of 1100 into 50 units of water; after allowing to dissolve by heating, allow it to cool to 50°C, then mix 50 units of 10% potato starch. Furthermore, add 30 units 50% [illegible], 10 units of 37% formalin, and polyethylene glycol having a molecular weight of 1,000 in a quantity shown in Table 1. After thoroughly mixing the ingredients, the reaction raw material liquid is prepared.

Next, the solution is poured into a mold made of Hourou [transliteration] with dimesions of 10 cm (length) x 25 cm (width) x 7 cm (height), and the formal reaction is carried out by heating at 45°C for 40 hours.

The produced sponge is introduced into a bath containing 10 units of 37% formalin, 30

units of 20% [illegible], and 110 units of water at a temperature of 50°C, and the reaction is carried out for 10 hours.

The resultant porous body is washed with water and allowed to dry in a ventilating dryer at 100°C, and the dry [illegible] PVAt porous body is obtained.

The, water absorbing property and quick-water-absorbing property after rinsing with water are measured for the treated porous body, and the condition of the airholes is checked. The obtained results are shown in Table 1.

For comparison purposes, the case of adding polyethylene glycol at the late stage and the case of adding glycerine or diethylene glycol in place of polyethylene glycol [illegible] PVAt porous body and glycerine or diethylene glycol added at the late stage are tested identically; the obtained results are also shown in Table 1.

The speed of water absorption is judged by testing the water absorbing rate. Namely, the product dried in a ventilated dryer at 100°C [illegible] is soaked in a water bath at 20°C; after leaving it inside for 5 minutes, it is taken out of the water and placed into a washer called "Blue Sky" made by Hitachi for spin; drying for 5 minutes. The water absorbing rate is calculated by the following formula:

Water absorbing rate = sponge weight after centrifugal dehydration – dry sponge weight / dry sponge weight x 100

Also, the rinse test is conducted using the above-mentioned Blue Sky washer at the bath rate of 50:1 for 15 minutes. Next, it is allowed to dry [illegible] at 100°C. Airhole uniformity is checked by naked-eye observation using a low-magnification microscope, and the range of average airhole diameters was observed.

Table 1

No.	Additives			Water absorbing rate (%)				Average airhole diameters (μ)
	Name	Amount of additives [illegible]	Method of addition	Before rinsing	After rinsing			
					One time	Three times	Five times	
1. Comparison	-	0	-	5	6	5	6	160 ~ 200
2."	PEG	0.5	Add [illegible] solution	17	15	18	16	150 ~ 200
3. Application	"	1.5	"	74	71	68	70	160 ~ 200

example of the present invention								
4. "	"	5	"	113	104	107	101	160 ~ 220
5. "	"	10	"	120	109	112	107	160 ~ 210
6. "	"	20	"	125	116	116	105	170 ~ 220
7. "	"	30	"	122	114	110	111	160 ~ 230
8. Comparison	"	40	"	123	117	115	103	150 ~ 250
9. "	"	10	Post addition treatment	125	41	14	11	160 ~ 200
10. "	Glycerine	"	Stock solution addition	8	7	8	7	150 ~ 200
11. "	DEG	"	"	7	8	6	6	"
12. "	Glycerine	"	Post addition treatment	145	56	29	15	160 ~ 200
13. "	DEG	"	"	138	50	24	12	"

It is clear from Table 1 that the long-term performance can only exist when polyethylene glycol is added to the raw material solution. Also, it is only effective when the addition quantity is within a certain range. In Table 1, PEG represents polyethylene glycol and DEG represents diethylene glycol.

Application Example 2

A mixture having an equimolar amount of PVA with an average polymerization degree of 800 and PVA with an average polymerization degree of 1700 is dispersed into water, after dissolving by heating at 98°C, it is allowed to cool to 50°C. After adding a water dispersion solution of cornstarch to the liquid, it is mixed uniformly. This is, heated to 85°C while stirring for 30 minutes to allow the starch to form into a paste. Next, it is cooled to 40°C and water is

added. Thus a liquid containing starch [illegible] having 12% PVA is obtained. To the solution, PEG with various molecular weights shown in Table 2 is added at a ratio a 10 wt% with respect to PVA, and mixed thoroughly. Furthermore, 37% formalin is added so that 1.1 mol of formaldehyde to PVA* and 50% sulfuric acid is added to 50% pure sulfuric acid [sic] to PVA, then mixed uniformly. The reaction raw material liquid is thus prepared.

The reaction raw material liquid is placed into a stainless container, and an acetalation reaction is carried out at 60°C for 14 hours. The resultant substance is washed with water, the un-reacted substance is removed, and allowed to dry. The same test as in Application Example 1 is conducted, and the results are shown in Table 2.

Table 2

No.	Molecular weight of polyethylene glycol	Water absorbing property (%)				Average airhole diameter (μ)
		Before the rinsing [illegible]	After rinsing			
			One time	Three times	Five times	
1. Comparison	400	34	21	17	13	90 ~ 130
2. Application example of the present invention	600	115	108	104	105	"
3. "	800	127	116	119	112	100 ~ 140
4. "	1040	131	115	114	110	100 ~ 150
5. "	1400	98	92	88	90	90 ~ 140
6. Comparison	1700	52	43	33	27	100 ~ 140

It is clear from Table 2 that especially effective results are obtained within a certain range

* [This phrase should probably read: 37% formalin is added so that 1.1 mol of formaldehyde is present with respect to PVA.]

of contents of polyethylene glycol.

Application Example 3

The PVAt porous body is prepared identically to that in Application Example 2, except that the polyethylene glycol with a molecular weight of 1040 is used, and instead of formaldehyde and acetaldehyde as the aldehyde, darokiz [transliteration] or adipoaldehyde is used in an amount of 1.5 mol with respect to PVA.

The same tests as in Application Example 1 were conducted. The results are shown in Table 3

Table 3

No.	Aldehyde [illegible]	Water absorbing property (%)				Average airhole diameter (μ)
		Before the rinsing [illegible]	After rinsing			
			One time	Three times	Five times	
1.	Formaldehyde	125	119	112	106	100 ~ 150
2.	Acetaldehyde	108	105	101	102	90 ~ 160
3.	Glyoxal	162	155	153	147	"
4.	Adipoaldehyde	147	141	138	135	110 ~ 150

It is clear from Table 3 that compared with a monoaldehyde, a dialdehyde has superb quick-water-absorbing properties. Also, the already possessed excellent properties before the rinsing possibly includes the effective fixation property of the polyethylene glycol.

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PREPARATION OF QUICK-WATER-ABSORBING POLYVINYL ACETAL POROUS BODY

2110-A WHITE HORSE TRAIL, AUSTIN, TX 78757 Phone: (512) 343-8389
Toll-free: 877-452-1348, Fax: (512) 343-6721, Email: phoenixtranslations@ev1.net